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ELECTROBLASTING TECHNOLOGY FOR PRODUCING NANOPOWDERS OF HIGH-MELTING NONMETALLIC MATERIALS

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The results of studies characterizing the electric explosion (EEC) of conductors as a chemical reactor are described. It is demonstrated that an EEC in chemically active media can produce nanopowders of high-melting nonmetallic materials in a nanodispersed state. The conditions making it possible to control the phase, chemical, and dispersion compositions of powders are analyzed, such as energy supplied to the conductor, the arc stage, chemical composition, and the density of the ambient atmosphere.

High-melting compounds are widely applied in science and engineering due to such properties as their high hardness, wear resistance, elasticity, fire resistance, and chemical inertness. They are of interest for producing cutting tools, structural parts serving under high temperatures, alloy modifiers, or reinforcement of composites based on metals, alloys, or ceramics. Substantial improvements of functional material parameters can be achieved by using nanopowders (NP).

The various methods for producing nanopowders of metals and their chemical compounds can be reduced to two processes: formation of small particles from atoms, molecules, and clusters and dispersing solid bodies [1 – 4]. The most popular are the evaporation – condensation method and plasmachemical synthesis. When NP are produced by the evaporation condensation method, problems arise related to maintaining special requirements imposed on the heating zone and cooling. This method has a low output and involves high power consumption. The plasmachemical method of synthesizing high-melting compounds, despite its high output, also involves high energy consumption, has many stages, a wide interval of size distribution of particles, and a high content of impurities in powders, which is due to the protracted contact of the target powder with the decomposition products.

The electroblasting technology for producing nanopowders based on the phenomenon of electric explosion of conductors (EEC) has been extensely developed lately. The electric explosion of conductors is a nonequilibrium process in which a conductor under the effect of a pulse current becomes dispersed and mixed with the ambient medium. Thus, EEC as a method for NP production combines the properties of dispersion methods (the conductor is destroyed under the effect of electric current) and of the evaporation-condensation methods, since a substantial part of the conductor material during electric explosion initially transforms into a gaseous state.

The advantage of electric blast technology is its universality in producing diverse NP. During an EEC, nanopowders of metals, alloys, and intermetallic compounds are formed in an inert gaseous or hydrogen medium, whereas NP of metal and nonmetal (oxides, nitrides, carbides, etc.) compounds are formed in a medium of chemically active gases. The important advantages of this technology is the possibility of controlling the properties of target products of the electric explosion, i.e., the dispersion, phase, and chemical composition of the nanopowders and other properties by controlling the electric parameters. The electric explosion technology has low energy consumption, less than 10 kW · h/kg, and a high output (up to 300 g/h for tungsten carbide). The low energy consumption is due to the direct heating of the conductor in an electric current without a heat carrier and a high heating rate (over 10^7 K/sec), which provides nearly adiabatic conditions of energy transfer to the conductor.

The process of producing nanopowders by EEC occurs in an enclosed chamber, and there are no toxic emissions or waste, which confirms the environmental safety of this technology and makes it promising for industrial application.

Electroblasted NPs have several advantages over NPs produced by other methods: they have spheroid particles, are resistant to oxidation and sintering at room temperature, and have a high chemical and diffusion activity under heating,

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which is related to the metastable state of nanoparticles, with the possibility of their self-heating within a narrow localized reaction zone [5, 6].

In this paper we describe the most significant results of our studies characterizing the EEC as a chemical reactor and demonstrating the possibility of electric explosion technology for producing high-melting nonmetallic materials in a nanodispersed state.

Nanopowders of high-melting compounds have been obtained on a UDP-4G experimental-industrial plant (Fig. 1). The plant operates as follows. Capacity energy accumulator *2* is charged from high-voltage power source *1*. Wire feed mechanism *3* provides automatic feed of a wire segment *4* to be exploded between two electrodes. As the wire reaches high-voltage electrode *5*, switch *6* is switched on, and the accumulator sends a discharge to the wire segment, which explodes. The emerging powder is collected in container *7*. The gas cleaned from the powder is fed back into the chamber using fan *8*. The space of chamber *9* is vacuum-treated before the process and then filled with a particular gaseous atmosphere. These functions are fulfilled by gas supply system *10*. The gaseous atmosphere for producing nanopowders of high-melting compounds can be represented by various hydrocarbon gases, nitrogen, or oxygen-bearing gases. The electric contour parameters are as follows: capacitor battery capacity is 1 – 5 μF, charging voltage of the energy accumulator is 12.5 – 30.0 kV, and discharge contour inductance is 0.58 μH.

Nanopowders were obtained by blasting conductors of diameter 0.2 and 0.3 mm and length 0.06 – 0.10 m made of tungsten, titanium, tantalum, and aluminum. The electric explosion of conductors was performed in the "fast explosion" mode with an infinite current pause or with an arc stage. The power parameters of the process were controlled by varying the charge voltage, charge capacity, or the length of the conductor exploded. The specific energy supplied to the conductor varied from 0.6 to $2.0e_s$ (e_s is the sublimation energy of the conductor material) and the arc stage energy e_a varied from 0.5 to $1.6e_s$.

The semiquantitative phase analysis of powders obtained was performed using a DRON-3.0 x-ray diffractometer using CuK_α tube radiation. The dispersion and the shape of particles were identified by means of a JSM-840 scanning electron microscope and the specific surface area of powders was found by the method of low-temperature nitrogen adsorption (BET method).

The study of composition of the products of an electric blast of tungsten conductors in acetylene-argon and propane-argon gaseous media indicates that the obtained powders contain the phases β-WC (WC_{1-x}), W_2C, α-W, and β-W [7]. As the input energy of the conductor and the arc stage energy grow, the relative content of tungsten carbide W_2C, which is less carbide-saturated, decreases and the content of the phase WC_{1-x} grows (Table 1, samples 2 – 5). The high temperatures of synthesis of tungsten carbide in the course of electric explosion and the fast chilling of the resultant powder leads to the stabilization of the disordered metastable state of the carbide WC_{1-x}.

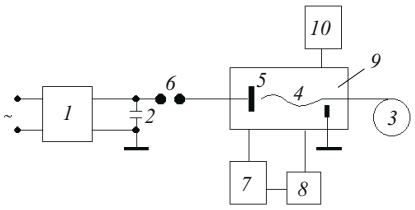

Fig. 1. Basic scheme of plant UDP-4G for producing nanopowders by the EEC method.

According to electron scanning microscopy data [7], the powder particles have a spherical shape of micron (1 – 6 μm) and submicron (0.1 μm and less) size. Tungsten carbide powders of a higher dispersion are formed under the effect of the electric arc formed after the proper explosion of the conductor (Table 1, samples 4 and 5): the specific surface area of powders obtained at $e/e_s = 0.9$ grows from 8.5 to 23.5 m^2/g as e_a/e_s grows from 0.4 to 1.5. The dispersion of powders is also increased as a consequence of the degree of dissolution of acetylene with argon decreasing from 9 : 1 to 4 : 1 molar ratio (Table 1, samples 1 and 4).

According to x-ray phase analysis, the final products of the explosion of titanium conductors in a propane-argon gaseous medium are carbide TiC and metallic α-Ti, and in an acetylene-argon medium only carbide TiC [7]. The spectral microscopic study of the products of electric explosion of titanium conductors in a gaseous hydrocarbon atmosphere indicates that the particles retain a spherical shape [7].

The powders obtained in the electric explosion of tantalum conductors in acetylene-argon mixtures contain the phases α-Ta_2C and TaC, as well as traces of metallic α-Ta [7]. The composition of the final products of electric explosion and specific surface areas of samples are given in Table 2.

The concentration of acetylene in argon has a perceptible effect on the phase composition of the target products. An in-

TABLE 1

Sample	e/e_s	e_a/e_d	Ar : C_2H_2	Phase composition	Intensity ratio of 100% reflections W_2C : WC_{1-x}	Specific surface area, m^2/g
1	0.9	0.4	9 : 1	WC_{1-x}, W_2C, α-W, β-W	0.55	4.9
2	0.7	0.1	4 : 1	The same	0.47	6.8
3	0.8	0.2	4 : 1	″	0.34	–
4	0.9	0.4	4 : 1	″	0.20	8.5
5	0.9	1.5	4 : 1	WC_{1-x}, W_2C, β-W	0.12	23.5
6	0.9	0.3	2 : 1*	WC_{1-x}, W_2C, α-W, β-W	0.59	4.7

* Ar : C_3H_8.

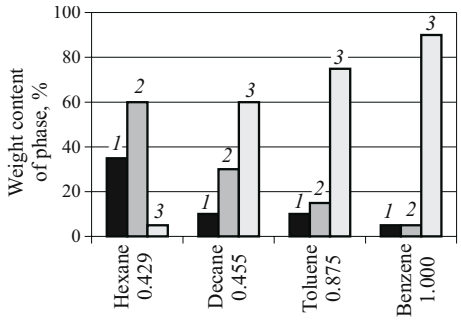

Fig. 2. Content of phases in the products of electric explosion of tungsten conductors depending on the C : H ratio in the hydrocarbon molecules: *1*) W; *2*) W_2C; *3*) WC_{1-x}.

creased content in the TaC phase compared to the phase α-Ta_2C is observed when the degree of dilution of acetylene in argon decreases from 9 : 1 to 4 : 1 molar parts (Table 2, samples 1 and 2, 3 and 4). With equal degrees of dilution of acetylene with argon, the content of the TaC phase grows with respect to the α-Ta_2C phase when the input energy and the arc discharge energy increase (Table 2, samples 1 and 3, 2 and 4). The specific surface area of the powders grows with increasing input energy and arc stage energy, as well as with an increasing concentration of acetylene in argon.

Tungsten, titanium, and tantalum carbides obtained by EEC in gaseous media have a carbon deficit and contain residual metal [7, 8]. To increase the yield of carbides and to obtain more carbon-saturated phases, it is advisable to increase the pressure inside the synthesis chamber, which is not always technically justifiable, or to use denser condensed hydrocarbon media in which it is possible to achieve a significantly higher concentration of carbon atoms than during an explosion in gases. The technological opportunities of electroblasting production of NP have increased due to the specifics of metals dispersing under a powerful current pulse and subsequent reactions between the products of the EEC and the ambient liquid or solid medium.

In [8, 9] we investigated the phase composition of NPs formed in electric explosions of tungsten, titanium, and aluminum conductors in condensed hydrocarbons, depending on the electric characteristics and chemical compositions of the hydrocarbons. The working media were the following liquid hydrocarbons: hexane, decane, bezene, toluene, as well as solid paraffin.

TABLE 2

Sample	e/e_s	e_a/e_d	Ar : C_2H_2	Phase composition	Intensity ratio of 100% reflections TaC : Ta_2C	Specific surface area, m^2/g
1	0.9	0.1	4 : 1	TaC, α-Ta_2C	4.57	6.3
2	1.0	0.1	9 : 1	TaC, α-Ta_2C, α-Ta	0.45	3.0
3	1.2	0.5	4 : 1	TaC, α-Ta_2C	4.74	13.4
4	1.3	0.4	9 : 1	The same	2.15	5.5

According to x-ray phase analysis data, the powders obtained in an electric explosion of tungsten conductors in liquid hydrocarbons contain the following phases: W, W_2C, and WC_{1-x}.

Ambient medium composition in EEC	Phase composition of EEC products
Hexane	W, W_2C, WC_{1-x}
Decane	W, W_2C, WC_{1-x}
Benzene	W, W_2C, WC_{1-x}
Toluene	W, W_2C, WC_{1-x}
Paraffin	WC

The qualitative composition of the products of electric explosion of tungsten conductors under about $1.2e_s$ input energy depending on the type of the liquid hydrocarbon is shown in Fig. 2. With increasing C : H ratio and increasing density of liquid hydrocarbon, the yield of tungsten carbide WC_{1-x} increases and the content of metallic tungsten decreases.

In the course of electric explosion of tungsten conductors in liquid hydrocarbons, even with the maximum energy input ($e/e_s = 1.2$) tungsten carbide is formed, which is a nonstoichiometric compound WC_{1-x} with a carbon deficit. The electric explosion of tungsten conductors in a solid saturated hydrocarbon, that is, paraffin, yielded the more carbon-saturated stoichiometric tungsten carbide WC [8, 9].

The dependence of the phase composition of powders produced in an electric explosion of titanium conductors in liquid hydrocarbon (decane) on the energy supplied to the conductor is established in [8]. As the energy grows from 0.7 to $1.3e/e_s$, the content of titanium carbide in the final products increases. The content of residual titanium is insignificant even with $e/e_s = 0.7$ and is equal to 15%, whereas with $e/e_s \geq 1.3$ the diffraction patterns exhibit only the reflections of carbide TiC.

Electron microscope studies of samples of the EEC products in liquid carbon-bearing media indicate that the particles retain their spherical shape [8, 9].

It is possible to obtain NP of a complex phase and chemical composition using EEC, provided that the upper temperature bounds of stability of the chemical compounds are close. If these values are different, the product formed will presumably be steady up to the higher temperatures. The products of electric explosion of aluminum conductors in a suspension of hexamethylenetetramine (urotropin $(CH_2)_6N_4$) in decane exhibit aluminum carbide, aluminum nitride, and aluminum that has not reacted (Fig. 3) [10]. The choice of urotropin as a reactant is due to its capacity to yield active nitrogen atoms under its thermal decomposition. The content of nitride was around 20%, which is presumably related to its lower thermal stability. Aluminum nitride is sublimated at a temperature of 2723 K [11].

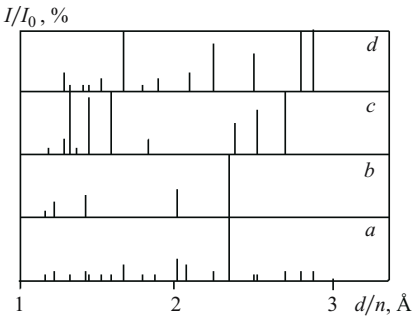

Fig. 3. Diffraction patterns of products of electric explosion of aluminum conductors in hexamethylenetetramine suspension in decane (*a*); ASTM data: *b*) Al; *c*) AlN; *d*) Al_4C_3.

A specific feature of electroblasted nanopowders is their metastable state; therefore, to use NP in various technologies, their stability in air should be estimated.

The activity with respect to air oxygen of tungsten carbide NP produced in the electric explosion of tungsten conductors in decane was estimated by differential thermal analysis under heating in an air medium, according to the following parameters: oxidation start temperature t_s, maximum oxidation rate v_{ox}, degree of transformation (the degree of oxidation) of powders α in a temperature interval up to 1000°C, and reduced (arbitrary) thermal oxidation effect, i.e., the ratio of the surface area of a peak on the heat emission curve (DTA) to the weight increase of the analyzed sample $S/\Delta m$. The specified parameters are listed in Table 3.

The degree of oxidation (the sample weight increment when heated to 1000°C) within the considered input energy range initially sharply grows with e/e_s, increases from 0.4 to 0.7, and then decreases more slowly. With increasing input energy and a growing degree of dispersion of EEC products, the temperature of active oxidation start grows from 480 to 570°C. With further increase in e/e_s, the oxidation start temperature decreases to 540°C. The dependence of the rate of oxidation of EEC products is analogous to the dependence of the degree of oxidation of samples and the intense oxidation start temperature on the heating temperature. The study of the thermal effects of oxidation of powders indicates that the maximum thermal effect corresponds to the products obtained with $e/e_s = 0.4$. The minimal thermal effect of oxidation is found in products obtained with $e/e_s = 0.5 – 0.7$.

The parameters of thermal stability of samples obtained in EEC, both in condensed and in gaseous hydrocarbons [7, 8] completely correlate with the dependence of the phase and chemical composition of powders on the input energy. As the input energy grows, the content of residual metal decreases and the yield of carbides increases.

Thus, an EEC in chemically active media can produce nanopowders of high-melting nonmetallic materials: carbides, nitrides, and oxides of metals. A most significant parameter determining the dispersion of nanopowders and the form of the function of the size distribution of particles is the specific energy content (ratio e/e_s). As the energy supplied to the conductor grows, the degree of dispersion of the end products of electric blast increases and their size distribution becomes narrower. The presence of the arc stage, as a rule, increases the degree of dispersion and decreases the content of residual melt in powders. The contents of chemical compounds in the target products of EEC depend essentially on the upper bound of their thermal stability and the duration of the interaction between the dispersion products and the ambient medium components.

TABLE 3

Sample	e/e_s	t_s, °C	α, %, up to 1000°C	v_{ox}, mg/min	$S/\Delta m$, %*
1	0.4	480	10.8	2.0	100
2	0.5	560	15.4	6.3	86
3	0.7	570	18.8	9.0	82
4	1.1	540	16.5	7.0	96

* Thermal effect of oxidation of sample 1 is accepted as 100%.

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